PP# 5F0427
7E0513

Petitions Control Branch and
Division of Toxicological Evaluation

October 13, 1964

Division of Food Standards and Additives

AF 15-946

Combined prefile reviews of PP #5F0426 and PP #5F0427, "Trizone" on various crops.

The Dow Chemical Company proposes the inorganic bromide tolerances tabulated below for residues resulting from soil fumigations with "Trizone," a mixture containing 61% methyl bromide, 30% chloropicrin, and 9% propargyl bromide (6.8% 3-bromopropyne and 2.2% related brominated C_3-hydrocarbons).

Crop	Inorganic Bromide Tolerances (ppm) from propargyl bromide	from methyl bromide
broccoli	5	15
muskmelons	5	15
peppers	5	15
pineapples	5	15
strawberries	5	15
cauliflower	15	25
tomatoes	15	25
eggplant	20	40

PP #5F0426 pertains to 3-bromopropyne and PP #5F0427 to methyl bromide, each in combination with the other as components of the Trizone mixture. The same data are given in both petitions and we have accordingly combined the prefile reviews.

The petitioner has not proposed combined numerical tolerances, but proposes instead to amend Sec. 120.3 (erroneously given as Sec. 130.3) to provide that where a mixture of propargyl and methyl bromides is used, the overall quantity of inorganic bromide to be tolerated shall be the sum of the individual tolerances, in the same agricultural commodity, for propargyl and methyl bromides. Since there is no practical way to distinguish the individual residues of the two bromide fumigants, it would seem advisable to combine the individual tolerances directly in one regulation. Whether this should be done in this manner or as proposed by the petitioner can be decided after the final review.

The petitioner has stated claims that the mixture is a more effective fumigant than either methyl bromide or propargyl bromide alone and that the proportions used are critical. The amount of chloropicrin present is much lower than the maximum shown in the USDA Summary of Registered Agricultural Pesticide Chemical Uses for chloropicrin alone when used as a pre plant soil fumigant.

Although chemical abstracts uses "3-bromopropyne" for this compound, "propargyl bromide" is favored by industry and appears on a number of labels registered with the USDA. Either name is acceptable but 3-bromopropyne is preferred.

Conclusions

Adequate data are available to:

1. evaluate the residue methods. No try-out is required.
2. determine the possibility of residues of the fumigants per se on the crops. A preliminary evaluation indicates no 3-bromopropyne residues by a method sensitive to about 0.01 ppm.
3. estimate the maximum likely inorganic bromide residues in all the above crops.
4. estimate potential residues of inorganic bromide in meat and milk from the feeding of pineapple bran.

Recommendation

If toxicological considerations permit, we recommend that these two petitions be filed.

A preliminary review of the data indicates that 15 ppm from 3-bromopropyne and 25 ppm from methyl bromide would be more appropriate tolerances for muskmelons than those now proposed.

Detailed Considerations

Proposed Usage

Preplant applications are to be made at rates of 160-200 lbs Trizone/A by injecting to a depth of 4-6 inches into the soil with a special chisel-type applicator. Treated areas are to be covered with polyethylene film and exposed to the fumigant for at least 48 hours (longer depending on temperature). The original directions called for aerating 2-3 weeks for transplants, and 3-4 days for seeds.

At a conference held September 22, 1964, we pointed out that the supporting data did not reflect the shorter aeration period for seeding and that the USDA Summary required at least 7 days aeration for chloropicrin (alone). In new labelling submitted September 25, 1964, a uniform 2-3 weeks preplant interval is proposed for these crops.

Residue Methods

The petitioner has developed a gas chromatographic method for determining residues of 3-bromopropyne. The crop is macerated with water and extracted with benzene. An aliquot of the extract is injected without cleanup into a gas chromatograph equipped with an electron capture detector. The validation data on this procedure are adequate for final review. The petitioner claims a sensitivity of 0.1 ppm but we estimate tentatively that the sensitivity is actually about 0.01 ppm.

The original petitions contained no methods for residues of the fumigants methyl bromide and chloropicrin per se. We raised the question of chloropicrin residues at the September 22, 1964, conference and the petitioner sent us a method for chloropicrin. The procedure involves macerating the sample, acidifying, heating in a closed system and trapping chloropicrin in absorber tubes containing isopropyl alcohol and sodium peroxide. Refluxing the alcoholic solution converts chloropicrin to nitrite which is determined colorimetrically after a Bratton-Marshall reaction. The validation data presented on this method are adequate for final review.

Some of the inorganic bromide residues were determined by Dow's X-ray fluorescence method. The sensitivity of this method, as reported by the petitioner, is only 5 ppm. Since the numerical level of the combined proposed tolerances is at least 4 times the sensitivity level, the data obtained by this method are considered acceptable.

There are other data, for these crops, obtained by the method of Shrader et al, Ind. and Eng. Chem. 14, 1 (1942). This is similar to our enforcement method for present bromide tolerances and is adequate for obtaining residue data. No method try-out is necessary.

Residue Data

Organic Residues

3-Bromopropyne residue assays were run on each crop. The treatments reflected the proposed use, except in the case of pineapples which were treated with pure 3-bromopropyne instead of the mixture. A few samples of peppers, eggplant, muskmelons, and strawberries appear to have residues ranging from 0.01-0.05 ppm, by a method sensitive to about 0.01 ppm. The petitioner claims that these results are due to contamination. A preliminary evaluation indicates that the claim may be justified.and that probably there are no residues of 3-bromopropyne in these crops.

As originally presented, the petitioner relied on the findings of the 1950 hearings to support the presumed absence of methyl bromide and chloropicrin residues. We considered this adequate for the more volatile methyl bromide, but we were reluctant to rely solely upon the findings of the hearings in regard to chloropicrin. At our request at the September 22, 1964, conference, the petitioner sent us residue data on crops grown in soils which had been fumigated with chloropicrin. These data include residue studies on white potatoes, sweet potatoes, and strawberries. The doses involved exceed the chloropicrin portion of the proposed Trizone applications. While only one of these three crops, strawberries, is involved in the pending petition, we would expect potatoes to have a greater tendency to acquire chloropicrin residues than the crops in the petition. Therefore, we consider these studies adequate to determine the possibility of chloropicrin residues resulting from the proposed use.

Inorganic Bromide Residues

Crops were grown in soil treated with 3-bromopropyne and Trizone. The residues due to methyl bromide were calculated by difference.

Broccoli and Cauliflower

Only one study is available for each of these crops. However, the combined data constitute a reasonable basis for estimating residues and we conclude that the data on these two crops are adequate for final review.

Muskmelons

We consider the data for this crop in three studies conducted in Michigan and New York adequate for final review. From the high residues reported (combined max. 35 ppm, avg. 24 ppm) it would appear that the petitioner underestimated the tolerances needed for this crop. Fifteen and 25 ppm would be more appropriate than the levels of five and 15 ppm actually proposed.

Peppers

Three studies are reported for New York and Michigan and overall we consider the pepper data adequate for final review.

Pineapples

Two of the three Hawaiian studies with Trizone reflect preplant intervals of more than two weeks. The long growing season for this fruit makes this deficiency a minor one. In addition, the data are supported by three studies involving Brozone (69% methyl bromide, 1.4% chloropicrin, and 30% petroleum hydrocarbons) and two studies involving 3-bromopropyne alone.

Another study with ethylene dibromide is not pertinent to the proposed use. We consider these data adequate for final evaluation.

Strawberries

Seven studies in Maryland, New York, and California are of limited value because of preplant intervals exceeding 14 days. Four other studies in Michigan and New York with the support of the first group are adequate for final review.

Tomatoes

Four studies in Michigan and New York provide adequate data for final review.

Eggplant

Only two studies in Michigan and New York are available. Since this is a minor crop, we consider these data to be adequate. The combined individual tolerances proposed for eggplant is the only instance where the 50 ppm inorganic bromide tolerance on the same crops for residues resulting from soil fumigation with Nemagon would be exceeded.

Residues in Meat and Milk

The feeding of pineapple bran to cattle could cause inorganic bromide residues in meat and milk. However, the combined individual tolerances proposed for pineapple would yield residues in bran no greater than those from pineapple grown in Nemagon-treated soil. This question was discussed in detail in the (FSA (J. Alpert) memo of 2/18/63 in PP #294).

Other Considerations

The use of tomatoes grown in Trizone-treated soil may result in higher than tolerance level residues in concentrated tomato products. These residues would be within the 250 ppm inorganic bromide tolerance established by PAP 78S2 for residues resulting from Nemagon. We defer to PCE on the need for a food additive regulation to cover similar residues from Trizone.

In view of the volatility of these fumigants and the solubility of inorganic bromide compounds, we would not expect residues to build up in the soil. There are some limited data on soil residues from ethylene dibromide in PP #34 which may be pertinent to our final evaluation.

J. Wolff

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TE
JWolff:hmg
RD Init JAlpert
[illegible] (PP #4F0426;5F0426;5F0427;PAP #7S2)

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Petitions Control Branch and
Division of Toxicological Evaluation

August 31, 1966

Pesticides Branch, Division of Food
Standards and Additives

PP #7E0513. DBCP in watermelons. Evaluation of analytical methods and residue data.

The Technical Committee of the Interregional Research Project No. 4 visited to check the use of the nematocide 1,2-dibromo-3-chloropropane (DBCP, Fumazone, Nemagon) for use in the culture of watermelons. Accordingly the Committee proposes, under Sec. 408E, the establishment of a tolerance of 50 ppm for residues of inorganic bromide resulting from this use.

There is also a current tolerance of 75 ppm in all melons (including watermelons) for residues of inorganic bromide resulting from soil fumigations with ethylene dibromide.

The Shell Chemical Company originally proposed a tolerance of 50 ppm on all melons for residues of inorganic bromide from DBCP in connection with [illegible]. Since no data were available for watermelons the tolerance, when established, was limited to cantaloupes, muskmelons, and honeydew melons.

In April 1965, (see PP #5G0448) the present petitioner proposed the establishment of a temporary tolerance of 50 ppm on watermelons for inorganic bromide residues from DBCP. The data, consisting of a summary of one study in California, were meager. In addition, the lateness of the request precluded adequate consideration of the proposal, for that growing season and we were unable to recommend in favor of the then proposed temporary tolerance.

The present submission includes an amply detailed additional study from a second State -- Maryland.

Conclusions

1. There is no reasonable expectancy that any residues of inorganic bromide would result from the proposed use.

2. An adequate method is available to enforce the proposed tolerance.

3. When the pesticide is used as directed, residues of inorganic bromide would not exceed the proposed tolerance. While in fact a lower tolerance might suffice, we are not in favor of such a lower tolerance for the reasons given under Residue Data.

4. Residues of inorganic bromide would not build up in the soil on the registered use of DBCP.

Recommendation

If toxicological considerations permit, we recommend that the proposed tolerance of 50 ppm for residues of inorganic bromide, calculated as Br, in or on watermelons be established.

Detailed Considerations

Proposed Use

The pesticide is to be applied in combination with fertilizer, between the rows at the time of planting. The rate is to be 3-5.5 lbs. technical EDCP (100% active) per acre. This is a somewhat lower rate than those used for other crops (see PP 6E94). Applications are to be made only when the temperature exceeds 60°F.

There is some ambiguity in the letter of 4/13/66 from W. H. Smith of the Dow Chemical Company to FDA, USDA in regard to the composition of the EDB fumigation granules used in preparing the pesticide-fertilizer mixture. However, the petitioner's intent is clarified in the specifications for the chemical. (We confirmed this in a telephone conversation with R. Cassell of Dow, Texas on 8/19/66).

Nature of the Residue

Data in PP 6E94 show that organic bromide residues do not occur in crops grown in soil treated with EDCP. These data are also applicable to watermelons. The results with EDCP are consistent with those from ethylene dibromide (PP 6E0) and Telone (PP 6E1042G,7). We conclude therefore that inorganic bromide is the only residue of concern and that there is no reasonable expectancy that any residues of organic bromide would result from the proposed use.

Analytical Methods

A modification of the chemical method of Mapes and Rhoades (Shell [illegible], 197; 1964) is currently used to enforce inorganic bromide tolerances. This method would be adequate for enforcing the proposed tolerance on watermelons and would be the method of choice for this purpose.

Most of the residue data were obtained by the neutron activation procedure of Curtis and Schmidt (J. Ag. Food Chem; 10, 236; 1962). Curtis and Tessler (J. Ag. Food Chem; 10, 232; 1962) made a limited comparison of analyses by this procedure and by the chemical method. The results are roughly comparable, neutron activation yielding somewhat higher values.

In the study by the Shell Chemical Company where the neutron activation method was used blank values for whole watermelons, rind and meat (pulp) also low in comparison to the proposed tolerance and range from 0.0-1.5 ppm. Recoveries on samples fortified with 10-25 ppm (presumably from an inorganic bromide salt) are satisfactory ranging(except for one value of 75%) from 90-115%.

We consider the neutron activation procedure to be adequate [illegible] obtaining residue data and for use as an alternate on bromide procedure. It is not the method of choice for this purpose however as most of the [illegible] laboratories are not equipped to use it.

In the study at the University of California (Davis) a polarographic procedure was used. No details of this method are provided in the petition. A single blank value of 1.1 ppm and a single recovery value of [illegible] are given.

[illegible]

In [illegible] study reported by the [illegible] Chemical Company [illegible] were treated as described under Proposed Use with the [illegible] - [illegible] mixture at rates of 3 and 6 lb Act/A, the higher rate being approximately double that recommended. At harvest, residues [illegible] from the [illegible] dose range from 1.5 - 2.4 ppm and those from the higher dose range from 1.1 - 4.3 ppm.

In the California study one residue value of 2.8 ppm is reported [illegible] treated with approximately 17 lb. Act/A in an overall application.

These results indicate a large margin of safety between the expected residues and the proposed 50 ppm tolerance. However, data in PP #[illegible] for other melons show that residues from DBCP are quite variable. (The results reported [illegible] for somewhat higher rates of application range from [illegible] ppm.) Although a lower tolerance might suffice in view of the limited data for this crop, and the known variability of residues from this pesticide, we consider the 50 ppm tolerance proposed for watermelons -- the same as that already established for other melons -- to be appropriate.

[illegible]

In our memo of 3/11/65 in PP #5F0426,7 we evaluated [illegible] ethylene dibromide applications in [illegible] the [illegible]. We concluded that inorganic [illegible] residues [illegible] not become additive in the soil. Similar considerations apply to the proposed use of DBCP and we would not expect inorganic bromide residues to build up in the soil on the repeated use of this soil fumigant.

Other Considerations

Data in the Shell Chemical Company study show that residues tend to concentrate in the outer part of the melon. Residues in the meat are only 1/3 of those in the rind and less than 1/2 of those in the whole watermelon. Thus a margin of safety is afforded by the fact that the portion of the crop that is most commonly eaten would have residues well below the tolerance level.

This use would not increase the bromide level permitted in the diet since there is already a 75 ppm tolerance for residues from ethylene dibromide.

J. Wolff

cc
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File 5F0427

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COMMISSIONER OF FOOD AND DRUGS

May 18, 1965

BRIEFING MEMORANDUM
Dow Chemical Company
Midland, Mich. (AF 15-946)

Drew M. Baker, Jr.
Petitions Control Branch, BSSE

"Trizone"
Pesticide Petition Nos. 5F0426 and 5F0427

"Trizone" is the Dow trade name for a soil fumigant formulation containing methyl bromide, propargyl bromide, and chloropicrin. The attached order is a new pesticide regulation to provide for the safe use of "Trizone" on eggplants, muskmelons, tomatoes, broccoli, cauliflower, peppers, pineapples and strawberries. The order establishes tolerances for the residues of inorganic bromides (calculated as Br) that result from the proposed use of "Trizone." As amended by the petitioner the tolerances requested for inorganic bromides are 60 ppm on eggplants, 40 ppm on muskmelons and tomatoes, 25 ppm on broccoli, cauliflower, peppers, pineapples, and strawberries.

The Pesticides Regulation Division, ARS, USDA, has certified usefulness of "Trizone" for the purposes for which tolerances are sought. They find that the proposed tolerances reasonably reflect the amount of residues likely to result from the proposed usage.

The Division of Food Standards and Additives finds that the analytical method proposed in these petitions is adequate for enforcement of the proposed tolerances. They find that the residues of inorganic bromide from the use of "Trizone" as proposed in the petition will not exceed the proposed individual tolerances. They find that there will not be any residues of methyl bromide, propargyl bromide, or chloropicrin per se from the proposed usage.

Since there is no means of distinguishing the individual sources of the inorganic bromide residues, they recommend that the regulation be based on the combined residues from the proposed use of "Trizone." They find that the feeding of bran from pineapples grown in fumigated soil would not result in residues in meat (the bran is not fed to beef cattle) and would increase the background bromide level in milk by less than 5 ppm. They conclude that inorganic bromide residues that would result from the establishment of the requested tolerances would not exceed previously established tolerances for inorganic bromides except on eggplants, where the increase would be from 50 to 60 ppm.

The Division of Toxicological Evaluation concludes that no hazard would exist by establishment of the requested tolerances since additional inorganic bromide would not be added to the human diet.

The Fish and Wildlife Service, USDI, has no objection to the establishment of the requested tolerances.

We recommend that the attached order be signed and published.

APPROVED:

F. J. McFarland
Assistant to the Director
Bureau of Scientific Standards
and Evaluation

Robert S. Roe, Director
Bureau of Scientific Standards
and Evaluation

cc: PCB FSA TE ACR GC(Hearing Clerk) FRW
PP 5F0426 PP 5F0427 DFO PI EWH(Temp tol bk)
DMBaker:mak 5/18/65 DMB:mcs 5/6/65
R/D Init: GJBeusch 4/21/65
OGFitzhugh 4/23/65

R/D Signed FJMcFarland; RSRoe by LLRamsey

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FSA

THE DOW CHEMICAL COMPANY
408 EXECUTIVE BUILDING
15TH & L STREETS, N.W.
WASHINGTON, D.C. 20005
202 · 296-1915

April 21, 1965

Mr. Drew M. Baker
Assistant to the Director
Bureau of Scientific Standards and Evaluation
Food and Drug Administration
Department of Health, Education and Welfare
Washington, D. C. 20204

Dear Mr. Baker:

Re: Pesticide Petition 5 FO 427
Residues of Inorganic Bromide from Use of
Methyl Bromide (Trizone)

In confirmation of our phone conversations of yesterday (20 April 1965), we are agreeable to the changes in tolerance levels which your evaluations recommend. Accordingly we would appreciate your making these changes in Section F of the subject petition as follows:

Cauliflower	- from 25 to 20 ppm
Pepper	- from 15 to 20 ppm
Pineapple	- from 15 to 20 ppm.

Yours very truly,

W. W. Sunderland
Government Affairs Department

cc: Pesticide Regulation Division, U.S.D.A. (2)
G. E. Lynn

PCB

APR 21 1965

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File PP 5F0427

Petitions Control Branch April 13, 1965

Dr. George E. Whitmore
Division of Toxicological Evaluation
Petitions Review Branch

Proposed residue tolerances on crops resulting from soil fumigation with, "Trizone". (See October 26, 1965 filing memo).

PESTICIDE PETITION NO's 5F0426 & 5F0427
(For Final Evaluation)

Dow Chemical Company
Midland, Michigan
(AF 15-946)

FSA's data review developed that:

1) Organic residues will not occur in the crops involved by the establishment of the requested tolerances.

2) Inorganic bromide residues that would result from the establishment of the requested tolerances would not exceed previously established tolerances for these crops.

It considers the low milk residue that is related to the requested pineapple tolerance of no concern.

CONCLUSION:

No hazard would exist by the establishment of these tolerances since additional inorganic bromide would not be added to the human diet.

INIT:HBlumenthal

cc:
TE
FSA
PP NO. 5F0426 & 5F0427
BSSE (data processing)

GEWhitmore:gmj 04/13/65

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Pesticides Chemical Branch and
Division of Toxicological Evaluation

Division of Food Standards and Additives

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File:
PP# 5F0427

PP #5F0426 and PP #5F0427 combined; Inorganic bromide tolerances for residues of "Trizone." Evaluation of analytical methods and residue data.

The Dow Chemical Company proposes in PP #5F0426 for residues of 3-bromopropyne, and in PP #5F0427 for residues of methyl bromide the following inorganic bromide tolerances for residues of the soil fumigant "Trizone". The latter is a mixture of 61% methyl bromide, [illegible] chloropicrin, and [illegible] propargyl bromide (6.3% 3-bromopropyne and [illegible] related [illegible] hydrocarbons).

	Proposed Bromide Tolerances (ppm)	
Crop	From 3-bromopropyne	From methyl bromide
Broccoli	5	[illegible]
Peppers	5	[illegible]
[illegible]	[illegible]	[illegible]
Strawberries	[illegible]	[illegible]
Cauliflower	[illegible]	[illegible]
Muskmelons	15	[illegible]
Tomatoes	[illegible]	[illegible]
Eggplant	20	[illegible]

A [illegible] ppm tolerance for inorganic bromide residues has been established for all of these commodities, except strawberries, from soil fumigation with 1,2-dibromo-3-chloropropane. A 30 ppm tolerance for inorganic bromide residues has been established on strawberries [illegible] with methyl bromide.

Conclusions

1. The inorganic bromide residues from 3-bromopropyne [illegible] and [illegible] may exceed the proposed tolerances. This [illegible], as there is no practical way to distinguish between residues from 3-bromopropyne and those from methyl bromide.

[redacted]

[redacted] the group with proposed tolerances of 5 and 15 ppm, [redacted] pineapples, could have methyl bromide residues in [redacted] combined residues in excess of 40 ppm but less [redacted]

[redacted] with proposed tolerances of 15 and 15 ppm, would have [redacted] less than 25 ppm, i.e., less than 5 from 3-bromo[redacted] than 25 from methyl bromide.

[redacted] would not result in residues of the fumigant [redacted]

[redacted] from pineapples grown in fumigated soil would [redacted] bromide residues in meat (the bran is not used for beef [redacted] would increase the background bromide level in milk by less [redacted] ppm, which ppm is the maximum expected from pineapples grown in [redacted] soil.)

[redacted] would not cause a build-up of bromide residues in [redacted]

[redacted]

The tolerances proposed for broccoli, cantaloupes, and eggplant are [redacted] Horticultural considerations permit, we recommend that [redacted]

Tolerances for cauliflower and tomatoes, 10 and 20 ppm respectively, would be more [redacted] for residues from 3-bromopropyne than the 5 and 15 [redacted]

For pineapples, 20 ppm would be a more suitable tolerance for [redacted] methyl bromide than the 15 ppm proposed.

For cucurbits (i.e., melons and squash), 5 and 20 ppm respectively, would be more suitable [redacted] residues from 3-bromopropyne and methyl bromide than the [redacted] proposed.

[redacted] means of distinguishing the individual sources of the [redacted] recommend that any ensuing regulation be based [redacted] residues from the bromide containing components of [redacted] With these in mind, the following tolerances would be [redacted]

15 ppm--broccoli, cauliflower, peppers, pineapples, and strawberries*

40 ppm--cucumbers and tomatoes

60 ppm--eggplant

*Although 25 ppm would be adequate for these crops, we recommend their [redacted] this group for administrative conveniences.

Were the petitioner to propose these tolerances, toxicological considerations permitting, we would recommend their adoption.

Detailed Considerations

Use

Preplant applications are made by soil injection at a rate of 160-200 lbs "Trizone"/A. Treated areas are covered with film for 48 hours or more. The soil is then aerated for 2-3 weeks prior to planting or transplanting.

Residue Methods

Inorganic Bromide--Some of the data were obtained by the X-ray fluorescence procedure. This method, which was reviewed in our recent memo in PP #365, has a sensitivity of 5 ppm. We consider it adequate for obtaining the combined residues from "Trizone."

Most of the data were obtained by the method of Shrader, et al (Ind. Eng. Chem., 14, 1 (1942). This method also was reviewed in the aforementioned memo. It is sensitive to a few ppm although in the case of pineapples, blanks range up to 7 ppm. The last presumably is due to background bromide in the soil. This method is similar to our current enforcement procedure.

Chloropicrin--The petitioner's method involves acidifying and heating the macerated sample to release the fumigent, which is trapped in an isopropyl alcohol-water solution of sodium peroxide. On refluxing the chloropicrin is converted to nitrite, which is determined colorimetrically after a Bratton-Marshall reaction. Blanks on three crops range from 0.00-0.12 ppm and average 0.0% for sweet potatoes, 0.05 for white potatoes and 0.02 for strawberries. Recoveries range from 75-107% and average respectively 92, 85, and 88%.

We consider this procedure adequate for the determination of chloropicrin residues. In the unlikely event that an enforcement problem should arise, the polarographic method of Bark (see Anal. Chem., 34, 514 (1962) and J. Ag. Food Chem., 10, 158 (1962) could be applied to residues of chloropicrin and methyl bromide as well.

3-Bromopropynyl--The petitioner's method involves blending the macerated sample with water and extracting an aliquot with benzene. A portion of the extract is injected into a gas chromatograph with an electron capture detector. The petitioner states that the method has a sensitivity of 0.1 ppm, the lowest fortification used. Since this level gave a 20% scale deflection on peppers (vs 1.7% for the crop blank) where the ratio of benzene to sample was twice that in some other studies, we feel that 0.05 is a more reasonable, and still conservative, estimate of the sensitivity. Recoveries on all crops range from 83-101% and average about 90%.

Check analyses on samples which indicated possible residues were made by a modified procedure using an eight-fold increase in instrument sensitivity. Here we believe 0.01 ppm would be a conservative estimate of the method's sensitivity. Recoveries by the modified procedure on three crops range from 70-90 (av. 83)%.

We consider both versions of the procedure adequate for the determination of 3-bromopropyne residues.

Residue Data

Broccoli--In one study on this crop, residues from "Trizone" range from 5-15 ppm. Residues from 3-bromopropyne range from 1-2 ppm. This is within the proposed tolerances, but for administrative convenience, we suggest that this crop be included in the group with a combined tolerance of 25 ppm (5 ppm from 3-bromopropyne and 20 ppm from methyl bromide).

Peppers--Residue values from 3 studies in two states range from 6-20 ppm (uncorrected for blanks of 0 to >5 ppm) for "Trizone." Residues from 3-bromopropyne range from 0-2 ppm. Since the maximum value for the residue from methyl bromide is close to the proposed tolerance, here too we feel that 20 rather than 15 ppm would be a more suitable tolerance for methyl bromide or 25 ppm combined.

Pineapples--Most of the data in eight studies involve plants treated with "Brezone" (a similar soil fumigant containing methyl bromide) or 3-bromopropyne alone. Residues from 3-bromopropyne alone range up to 4 ppm, adjusted for exaggerated dosages. In the three studies with "Trizone," residues range from 7-21 ppm, uncorrected for blanks of 4-7 ppm. Since the last two values are right at the combined proposed tolerance level, and in view of the high blanks, here too we feel that 20 ppm would be a more suitable tolerance for residues from methyl bromide or 25 ppm combined.

Strawberries--Residues from 3-bromopropyne were 5 ppm in two studies but ranged from 1-8 (av. 5.5) ppm in a third study. This indicates that the 5 ppm tolerance for 3-bromopropyne may be inadequate. As noted above, this is rather academic. Data in 11 studies from four states show residues from "Trizone" ranging from 1-18 ppm. While the combined 20 ppm tolerance proposed seems adequate, for administrative convenience, we suggest that this crop be included in the group with a 25 ppm tolerance.

Cauliflower--Four residues from 3-bromopropyne range from 0-3 ppm; one value is 24 ppm. We agree with the petitioner that the 24 ppm value is aberrant and that residues from 3-bromopropyne would not exceed 5 ppm. The one available "Trizone" study contains six residue values for "Trizone" ranging from 12-24 ppm. Half of this range is due to the difference between 24 ppm and the next highest value of 18 ppm. This leads us to conclude that

this value too is probably aberrant. Omitting the 24 ppm value from "Trizone," the average residue is 16 ppm (17 if it is included). Therefore, we conclude that tolerances of 5 and 20 ppm (or 25 ppm combined) rather than the 15 and 25 ppm proposed would be adequate for cauliflower.

Muskmelons--Three studies from two states are reported. Residues from 3-bromopropyne range from 3-10 ppm. Residues from "Trizone" range from 11-35 ppm. In the study with the highest residues, the range is 21-35 (av.31) ppm uncorrected for a 1 ppm blank. The 15 and 25 ppm tolerances (or 40 ppm combined) proposed are adequate.

Tomatoes--Four studies from three states are reported. Residues from 3-bromopropyne range from 0-4 ppm in three studies and 1-15 ppm in another. The last is right at the proposed tolerance level. Residues from "Trizone" range from 1-37 ppm. In the study with the highest residues, the range is 18-37 (av.28) ppm uncorrected for a 1 ppm blank. The 15 and 25 ppm tolerances (or 40 ppm combined) proposed for tomatoes are adequate.

Eggplant--Two studies from two states are reported. Residues from 3-bromopropyne range from 1-11 ppm. In one study, residues from "Trizone" range from 18-27 (av.22) ppm. In the other study, the range is 38-55 (av.46) ppm. The 20 and 40 ppm tolerances (or 60 ppm combined) proposed for eggplant are adequate.

Organic Residues

Methyl Bromide--The high volatility and reactivity of this fumigant component renders the persistence of its residues extremely unlikely.

Chloropicrin--In a supplemental study submitted by the petitioner, white potatoes from soil treated with 70-210 lbs/A (vs. about 60 lbs/A in "Trizone") showed no residues. The crop was harvested 3½ months after treatment. Similarly in two studies with sweet potatoes, application rates were 260-315 and 175-265 lbs/A, respectively. The crops harvested in less than nine months in one case, and after about seven months in the other, showed no residues. Strawberry studies in two states involved 455 lbs/A treatments. No residues were found after 9 and 14 months, respectively.

On the basis of these data, we conclude that the proposed "Trizone" usage will yield no residues of chloropicrin in food crops.

1,3-Dichloropropene--Residue analyses for this fumigant component were made at the same time that inorganic bromides were determined. No residues of 3-bromopropyne per se were detected on broccoli, cauliflower, pineapples, or tomatoes. In one study on strawberries, seven samples showed no residues; in another study, three samples out of 17 showed apparent residues of 0.02 ppm. In one pepper study, 12 samples showed no residues; but in another study five samples out of nine showed residues of 0.01-0.02 ppm. On muskmelons, one sample out of 14 showed residues of 0.01 ppm and

on eggplant two studies out of nine showed residues of 0.02-0.05 ppm. All of these residue values are within the estimated 0.05 ppm sensitivity of the method used.

An investigation of the source of these apparent residues was undertaken using a method of higher sensitivity. The petitioner claims that the residues were due to contamination from 3-bromopropyne stored in the same freezer as the samples. In support of this claim, he shows that in the check analyses both control and treated samples show residues, with greater residues in the outer part than in the cores of eggplants and muskmelons. In addition, air samples taken from the freezer showed 3-bromopropyne and stored bottles of benzene picked up the equivalent of 0.08 µg/ml. While the data do indicate higher residues on treated than on control samples in three cases and lower in a fourth case, this could be due to chance.

Considering the above, we agree that the residues were due to contamination. Based on experience with similar fumigants (see Chloropicrin above), we would not expect this material to persist in the soil, get into young plants, and remain there until the crops are ripe. However, if such residues were to be present, they would be present at levels below 0.05 ppm.

Residues in Meat and Milk

The possible increase in background bromide levels in meat and milk from the feeding of pineapple bran was discussed in detail in the FSA (J. Alpert) memo in PP 3F0426 (Newsom). We reaffirm the finding made there that the feeding of pineapple bran would not yield residues in meat--this commodity is not fed to beef cattle--and would increase the bromide levels in milk by less than 2 ppm. The last is based on an estimated 9 ppm maximum increase due to the use of Newsom treated pineapple where the inorganic bromide tolerance is 50 ppm vs. the 25 ppm contemplated here.

Soil Residues

Naturally occurring bromides are believed to be tightly held by the anion exchange capacity of soils. Thus some bromide persists through leaching by rain. The addition of bromide beyond the anion exchange capacity of the soil would make it available for plant pick-up and leaching.

One soil study is given in PP #34. There soil was treated with "Dowfume W-85" (85% ethylene dibromide). The amount of bromide potentially available from the treatment used would exceed that from the use of 200 lbs/A of "Trizone." In addition the lower volatility of ethylene dibromide as compared to methyl bromide would tend to keep it in the soil longer. Overall, we would expect the residues from "Dowfume W-85" to exceed those from "Trizone."

In the study, four plots 30' x 28' were treated with 12 gals of "Dowfume W-85"/A. After 45 days samples were taken by compositing 12 soil cores (3/4" x 8") collected criss-cross of the plots. Blanks ranged from 10-30 (av.16) ppm and treated samples ranged from 12-19 (av.15) ppm. These results indicate no buildup of soil residues. However, in PP #5F0429, currently being reviewed, there is some indication of a slight increase in soil residues from ethylene dibromide treatments.

While the data are meager and conclusions must be based on analogy--we consider this a reasonable showing that the proposed use of "Trizone" would not cause bromide residues to become additive in the soil.

Other Considerations

There is a 50 ppm tolerance on all of these commodities, except strawberries, for inorganic bromide residues resulting from soil fumigations with Nemagon. Thus the proposed use would contribute lower bromide residues to all of these commodities except strawberries and eggplant. The former, however, has a 30 ppm tolerance (higher than the 25 contemplated here) for residues from post-harvest fumigation with methyl bromide. While the 60 ppm proposed for eggplant exceeds the present 50 ppm tolerance, this food is a very minor part of the diet.

The bromide level in concentrated tomato products might exceed the 40 ppm tolerance on the raw commodity. However, a 250 ppm tolerance has been established on concentrated tomato products in connection with the 50 ppm tolerance on raw tomatoes from Nemagon (FAP #782). The proposed use would thus yield lower residues and probably not require a modification of the Food Additives Regulations.

In the petitioner's method for the determination of 3-bromopropyne, an aqueous macerate is extracted with benzene. To ensure complete extraction of fumigant from the substrate, isopropyl alcohol should have been used as a bridge between the organic and inorganic phases. Since the recoveries were satisfactory, and since most of the fumigant would be extracted under the conditions used, we have no serious reservations about the method--for the purpose of showing the absence of residues.

J. Wolff

cc:
RDI(2)
TR
SF(Jones)
FSA/CB
FSA/PB (PP #5F0426; #5F0427; #5F0429; #345; #294; #34)
(FAP #782)
JWolff:jrf 3/11/85
RD-I: Allen

End of Document

FSA

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
PESTICIDES REGULATION DIVISION
WASHINGTON, D. C. 20250

file: pp#5F0427

JAN 8 1965

60 day 3/12/65
90 day 4/9/65

To: Frank J. McFarland, Assistant to the Director, Bureau of Scientific Standards and Evaluation, Food and Drug Administration, Department of Health, Education and Welfare

From: Justus C. Ward, Director, Pesticides Regulation Division

Subject: Certification of usefulness of the pesticidal chemical, methyl bromide, when used in combination with propargyl bromide and chloropicrin for use in treating soil to be planted to broccoli, cauliflower, egg plant, peppers, tomatoes, muskmelons, strawberries and pineapples.

On November 18, 1964, a copy of petition No. 5F0427 was filed proposing a tolerance for residues of inorganic bromides resulting from soil fumigation with methyl bromide when used in combination with propargyl bromide and chloropicrin. This combination of fumigants is to be used for controlling nematodes, weeds and soil borne disease fungi of broccoli, cauliflower, egg plant, peppers, tomatoes, muskmelons, strawberries and pineapples. The petition was submitted to you by the Dow Chemical Company, Midland, Michigan.

Pursuant to Section 408 (1) of Public Law 518 (68 Stat. 511), July 22, 1954, the petition and related data have been analyzed. It is hereby certified that the pesticidal chemical is useful for the purposes for which tolerances are sought.

Justus C. Ward

FSA

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
PESTICIDES REGULATION DIVISION
WASHINGTON 25, D.C.

CAN 8 285
60 days 3/12/65
90 days 4-9-65

To: William Stokes, Assistant to the Director
BSSE, Food and Drug Administration
Department of Health, Education, and Welfare

From: Justus C. Ward, Director
Pesticides Regulation Division
ARS, U. S. Department of Agriculture

Subject: Pesticide Petition No. 5F0427 requesting tolerances for methyl bromide, submitted by Dow Chemical Company, Midland, Michigan, and filed November 18, 1964

We have completed our examination of the residue data, analytical methods employed, and other pertinent information contained in this petition for tolerances of 40 parts per million (p.p.m.) in or on eggplant, 25 p.p.m. in or on cauliflower, tomatoes, and muskmelons, and 15 p.p.m. in or on broccoli, peppers, pineapples, and strawberries for residues of inorganic bromide resulting from the use of methyl bromide.

In accordance with the requirements of Public Law 518, 83rd Congress, we herein offer an opinion as to whether the proposed tolerances reasonably reflect the amount of residue likely to result when this pesticide chemical is used as proposed.

It is the opinion of this Department that the proposed tolerances reasonably reflect the amount of residue likely to result.

This opinion is based on the consideration that the methyl bromide will be used in combination with propargyl bromide and chloropicrin. The total residue of inorganic bromide likely to result is reflected by the sum of the tolerances for propargyl bromide and methyl bromide.

Justus C. Ward

Growth Through Agricultural Progress

End of Document

THE DOW CHEMICAL COMPANY
POST OFFICE BOX 512
MIDLAND, MICHIGAN 48641

Pesticide Petition No. 5F0427

December 28, 1964

Mr. Drew M. Baker (3)
Bureau of Scientific Standards and Evaluation
Food and Drug Administration
Washington, D. C. 20204

Dear Mr. Baker:

Your letter of November 18, 1964, and a telephone call from Mr. Robert L. Caswell of the Pesticides Regulation Division, USDA, have called to our attention a discrepancy between the residue data for muskmelons and the tolerances requested in our petitions for tolerances of inorganic bromide resulting from soil fumigation with TRIZONE, a combination of propargyl bromide, methyl bromide and chloropicrin.

We find that we inadvertently overlooked the data in Table 2. E, page 13, part D-4, which indicates that the proper proposed tolerance should be:

15 parts per million inorganic bromide from propargyl bromide
25 parts per million inorganic bromide from methyl bromide.

We request that Section F of the petition be so revised.

Sincerely,

G. E. Lynn
Director, Registration Section
Bioproducts Department

abc

cc: PRD/ARS/USDA Attention: Mr. Robert L. Caswell

End of Document

File

Pesticide Petition No. 5F0427

AF 15-946

November 18, 1964

Mr. C. E. Lynn
The Dow Chemical Company
Post Office Box 512
Midland, Michigan 48641

Dear Mr. Lynn:

We have completed our preliminary review of Pesticide Petition No. 5F0427 which proposes tolerances for residues of inorganic bromides (calculated as Br) in or on the following raw agricultural commodities grown in soil treated with methyl bromide:

40 parts per million on eggplant.
25 parts per million on cauliflower and tomatoes.
15 parts per million on broccoli, muskmelons, peppers, pineapples and strawberries.

The above residues result from the use of methyl bromide in combination with propargyl bromide. Our preliminary review indicates that 25 parts per million would be a more appropriate tolerance for muskmelons than that proposed above.

Our preliminary review also indicates that residues in concentrated tomato products may exceed the proposed tolerance for tomatoes. Thus, it may become necessary to amend the food additive regulations to provide for such higher residues.

This petition is being filed today.

Sincerely yours,

cc: PCB FSA TE

DMBaker:lch:11/18/64
RD:DME:cr:11/6/64
Init. JAlpert 11/6/64
FJMcFarland 11/17/64
WStokes 11/6/64

Drew M. Baker, Jr.
Assistant to the Director
Bureau of Scientific Standards and Evaluation

cc: Pesticides Regulation Division, ARS, USDA

End of Document

File PP# 5F0427 FSA Branch

Petitions Control Branch Oct. 26, 1964

Dr. George E. Whitmore
Division of Toxicological Evaluation
Petitions Review Branch

Propargyl bromide and Methyl bromide.

PESTICIDE PETITION NO. 5F0426
PESTICIDE PETITION NO. 5F0427

Dow Chemical Company
Midland, Michigan
(AF 15-946)

The Dow Chemical Company proposes the inorganic bromide tolerances tabulated below for residues resulting from soil fumigations with "Trizone," a mixture containing 61% methyl bromide, 30% chloropicrin, and 9% propargyl bromide (6.8% 3-bromopropyne and 2.2% related brominated C_3-hydrocarbons).

Crop	Inorganic Bromide Tolerances (ppm) from propargyl bromide	from methyl bromide
broccoli	5	15
muskmelons	5	15
peppers	5	15
pineapples	5	15
strawberries	5	15
cauliflower	15	25
tomatoes	15	25
eggplant	20	40

Division of Food Standards and Additives prefile data review of these two petitions developed that probably no residues of the organic compound, 3-bromopropyne (propargyl bromide), would occur on raw agriculture crops if these requested tolerances were allowed.

The petitioner has furnished chloropicrin residue data and claims residues of chloropicrin will not occur from the use of this soil fumigant. The Division of Food Standards and Additives refers to the USDA sanction of the use of chloropicrin alone as a soil fumigant at higher dose rates than would occur from soil application of the involved compound, "Trizone."

PP No. SF0426
PP No. SF0427
Oct. 16, 1964

Provided Food Standards and Additives final review of these two petitions conclude that 3-bromopropyne and chloropicrin do not appear as significant residues in the requested tolerance crops; adequate inorganic bromide toxicity data are available for a final evaluation of these two petitions.

CONCLUSION:

These petitions are adequate for filing.

INIT: Blumenthal

cc:
FSA
FS
BEHE(Data Processing)
PP No. 426 & 427

CBWhitmore:amp 10-26-64

End of Document

Alpert
Beusch
Hoffff

October 2, 1964

AF 15-946

Pesticide Petition No. 5F0427

Mr. G. E. Lynn
Bioproducts Department
The Dow Chemical Company
Abbott Road Buildings
Midland, Michigan

Dear Mr. Lynn:

We have your letter of September 4, 1964, transmitting two copies of a petition for methyl bromide, and we have the corrected check for $2,475.

This petition has been designated Pesticide Petition No. 5F0427.

We also received your letter of September 25, 1964, transmitting four copies of the following reports:

A Study of Residues of Chloropicrin in White Potatoes and Sweetpotatoes Following Field Fumigation With PICFUME

A Study of Residues of Chloropicrin in Strawberries Resulting From Preplant Application of PICFUME

We have added two copies of the above reports to Pesticide Petition No. 5F0427 and the other two copies to Pesticide Petition No. 5F0426.

We note that in your letter of September 25, 1964, you requested a change in Section B to extend the aeration period prior to planting with seeds of the food crops to 2 to 3 weeks. This change will be made.

We will write you again when we have completed our preliminary review of this petition.

Sincerely yours,

Drew M. Baker, Jr.
Asst. to the Director
Bureau of Scientific Standards and Evaluation

cc: Pesticides Regulation Division ARS-USDA
cc: PCB FSA TE

DMBaker:rh 10/1/64

End of Document

FSA (Caeper)

THE DOW CHEMICAL COMPANY

POST OFFICE BOX 512
MIDLAND, MICHIGAN 48641

September 25, 1964

Mr. William Stokes (4)
Pesticide Branch
Food and Drug Administration
Department of Health, Education and Welfare
Washington, D. C. 20201

5F0426
File: 5F0427

Dear Mr. Stokes:

Attached are two reports of investigations we have conducted to determine if the fumigation of soil with chloropicrin results in residues in raw agricultural commodities. These reports are as follows:

* A Study of Residues of Chloropicrin in White Potatoes and Sweet Potatoes Following Field Fumigation with PICFUME®

and

* A Study of the Residues of Chloropicrin in Strawberries Resulting from Preplant Application of PICFUME®.

You will note that in the report on potatoes and sweet potatoes the dosage of chloropicrin is given in gallons per acre. Chloropicrin weighs 14 pounds per gallon. Thus the dosages given correspond to pounds per acre as follows:

gallons per acre	=	pounds per acre
10		140
12 1/2		175
15		210
17 1/2		245
18		250
22 1/2		315

As a result of these studies we concluded that soil treatment with chloropicrin would not result in residues in food crops. Your attention is directed to the results with the white and sweet potatoes, which in our view represented a maximum opportunity for residues since they are tuber and root crops.

* The attachments are filed in PP # 5F0426

We request that these data be made a part of the petitions recently filed for methyl bromide and propargyl bromide as used in combination with chloropicrin in our product TRIZONE.

We are also enclosing a revision of the conditions of the proposed use with respect to the food crops involved. This would extend the aeration period prior to planting with seeds of the food crops from 2 to 3 days to 2 to 3 weeks. This is being done to bring the labeling in line with the aeration periods used in the plots from which the residue samples were taken.

We trust this information and change in Section B of the petitions now makes them acceptable for filing.

Sincerely,

G. E. Lynn
Director, Registration Section
Bioproducts Department

cc: Pesticides Regulation Branch, U.S.D.A. (4)

abc

13544

R103075

Chemical:	**Methyl bromide; Propargyl bromide; Chloropicrin**
PC Code:	**053201; 068701; 081501**
HED File Code	**11500 Petition Files Chemistry**
Memo Date:	**10/26/2004**
File ID:	**00000000**
Accession Number:	**412-05-0090**

HED Records Reference Center
01/27/2005